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PAPER

Salt-doped block copolymers: ion distribution, domain spacing and effective χ parameter

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We develop a self-consistent field theory for salt-doped diblock copolymers, such as polyethylene oxide (PEO)–polystyrene with added lithium salts. We account for the inhomogeneous distribution of Li^+ ions bound to the ion-dissolving block, the preferential solvation energy of anions in the different block domains, the translational entropy of anions, the ion-pair equilibrium between polymer-bound Li^+ and anion, and changes in the χ parameter due to the bound ions. We show that the preferential solvation energy of anions provides a large driving force for microphase separation. Our theory is able to explain many features observed in experiments, particularly the systematic dependence in the effective χ-parameter on the radius of the anions, the observed linear dependence in the effective χ on salt concentration, and increase in the domain spacing of the lamellar phase due to the addition of lithium salts. We also examine the relationship between two definitions of the effective χ parameter, one based on the domain spacing of the ordered phase and the other based on the structure factor in the disordered phase. We argue that the latter is a more fundamental measure of the effective interaction between the two blocks. We show that the ion distribution and the electrostatic potential profile depend strongly on the dielectric contrast between the two blocks and on the ability of the Li^+ to redistribute along the backbone of the ion-dissolving block.

I. Introduction

Ion-containing polymers are promising materials for energy applications.[1–4] Electrochemical applications based on polymers take advantage of their ionic conduction[5] combined with mechanical properties.[6] In recent years, block copolymers with an ion-dissolving block, typically polyethylene oxide (PEO), and a non-conducting block such as polystyrene (PS), have received considerable attention as novel rechargeable battery materials.[3,6] Upon addition of lithium salts, the lithium ions are complexed with the EO groups,[7–9] and together with its counterions, provide the charge carriers for ion conduction.[10,11] The second, non-conducting block can be tuned to confer other functions, such as mechanical robustness[3,6,11] and the desired microstructures.[6,12–14]

Experimentally, the addition of lithium salts has been shown to have a drastic effect on the phase behavior of block copolymers.[15–21] Adding even a small amount of lithium salts (a few percent in the $[Li^+]/[EO]$ ratio) leads to an increase of the order–disorder-transition temperature by tens of degrees Celsius[15] and a significant expansion of the periodicity of the ordered phases (beyond the simple volume effects of the salt ions).[17,21] Even the topology of the phase diagram can be altered by the addition of the lithium salts.[16] A common conclusion from the body of the experimental work on lithium salt-doped block copolymers is that the addition of the salts leads to an increase in the effective parameter, χ_{eff}, that characterizes the unfavorable interaction between the constituent blocks. By examining the χ_{eff} for several lithium salts with different anions in PEO-PS block copolymers, Wanakule *et al.* found a systematic dependence on the radii of the anions,[20] which suggested a role of the Born solvation energy.[22] We have recently developed a theory[23] for ion-containing polymers such as lithium salt-doped PEO-PS that incorporates the Born solvation energy of the anions, together with other effects, such as the tight complexation between the Li^+ ion and the EO monomers, the altered monomer identity due to the Li^+ binding, the translational entropy of the anions, and the ion-pair equilibrium between the Li^+ ions and the anions. By studying the shift in the spinodal of the disordered phase using the random phase approximation, we are able to obtain a χ_{eff} in good qualitative agreement with experimental results. In particular, the theory captures the systematic dependence of χ_{eff} on the anion radius.

The goal of the present work is two-fold. First, we provide a more detailed exposition of our theory published in ref. 23. Second, and more importantly, we address a number of issues not addressed in our earlier work. While ref. 23 has established the conceptual framework, it has only studied the thermodynamics in the disordered phase. Here, we apply the full self-consistent field theory to the lamellar phase of the lithium salt-doped block copolymers to study the distribution of the Li^+ and anions, and the dependence of the lamellar spacing on the salt concentration. In addition, we examine the relationship between

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the effective parameter χ_{eff} determined from the shift in the spinodal in the disordered phase and that determined from the periodicity of the ordered phases.

Gomez *et al.*[11] studied the distribution of Li^+ ions in the ordered lamellar phase of the PEO-PS diblock copolymers using energy-filtered transmission electron microscopy techniques. An interesting observation is that the Li^+ ions appear to be localized in the middle region of the PEO domain, and that the width of this region increases at a slower rate than the domain spacing as the molecular weight increases. These authors explained the localization effect by showing a correlation of the width of the ion distribution with the spatially inhomogeneous stress field in the salt-free block copolymers,[24] but did not calculate the distribution of the ions. Here, we calculate the distribution of both the Li^+ and anions using the self-consistent field theory, which includes a treatment of the electrostatics with inhomogeneous self-energy of the ions.[25] Our results show that the distribution of the Li^+ ions and the anions, is a result of the combined effects of the stress field, the electrostatic potential, and to a significant degree, the solvation energy of the anions, and cannot be explained in terms of the inhomogeneous stress field alone.

Experimentally, the effective parameter χ_{eff} is obtained by mapping the properties of the salt-doped block copolymers (such as the domain spacing of the ordered phases) to the corresponding properties of the salt-free system. For salt-free block copolymers, a single Flory–Huggins parameter χ (for fixed molecular characteristics of the system, such as degree of polymerization and composition) describes all the properties of the system in both the ordered and disordered phases. In other words, the parameter χ can be obtained either by the behavior of the structure factor in the disordered phase, by the domain spacing in the ordered phases, or by the location of the phase boundaries; if the regression is done consistently, all properties will yield the same χ. On the other hand, the effective parameter χ_{eff} reflects the combined effects of several contributing factors, whose relative contributions may depend on the state of the system or on the properties studied. Therefore, χ_{eff} determined from the spinodal of the disordered phase using the random phase approximation[23] may not coincide with χ_{eff} determined from the domain spacing of the ordered phases. By the same reasoning, the χ_{eff} determined from the spacing of different ordered phases may not be the same, as recently observed by Young *et al.*[18] We find that the χ_{eff} determined from the spinodal of the disordered phase is generally larger than that determined from the lamellar spacing and exhibits a stronger dependence on the radii of the anions. We argue that the χ_{eff} determined from the spinodal of the disordered phase is a more fundamental measure of the effective interaction between the two blocks.

The rest of this article is organized as follows. In Section II, we present a model for salt-doped block copolymers and develop a self-consistent field theory, using PEO-PS and lithium salts as a model system. In our model, we include (1) the tight complexation of the Li^+ ions with the EO groups, (2) the variable charge density of the PEO chains due to binding by the Li^+ ions, (3) the preferential solvation energy (Born energy) of the anions for the PEO domain, (4) ion-pair formation between the anion and the EO-complexing Li^+, and (5) change in the monomer-level interaction due to the binding of the Li^+ ions to the PEO. In Section III, we obtain the structure factor of the block copolymer in the disordered phase which allows us to identify the χ_{eff} from the shift in the spinodal. In Section IV, we study the lamellar structure as an example for the ordered phases, focusing on the distribution of the ions and the change in the lamellar spacing, and discuss the different definitions of χ_{eff}. In Section V, we briefly summarize our results and offer some concluding remarks.

II. Model

We consider n_c A–B diblock copolymers with the total degree of polymerization, N_c, and n_+ cations (Li^+), and n_- monovalent anions (X^-) in volume V. The degrees of polymerization for polymer A and polymer B are N_A and N_B, respectively, so the fractional composition of block A is given by $f_c = N_A/N_c$. The monomer volumes for A and B, and the volumes of Li^+ ion and anion are respectively v_A, v_B, v_+, and v_-. For easy reference to the polymers of interest in experiments, we refer to A as the PEO block and B as the PS block. However, in the numerical calculations, we do not use the molecular parameters specific to the PEO-PS systems. Rather, we consider a generic diblock copolymer with qualitatively similar interactions with the lithium salt as the PEO-PS, but with identical monomer volume and Kuhn length in the two blocks. Therefore, in subsequent discussions, the terms PEO block and PS blocks are not to be taken literally, but rather refer to PEO-like and PS-like blocks. Our rationale in considering a generic model is to highlight the effects of the added salts, such as electrostatic interactions, the translational entropy of the anions, and most importantly the solvation energy of the anions, without unnecessary complications due to effects of conformation asymmetry in the structure and phase behavior.[26]

Since the binding energy between Li^+ and oxygen is very large,[27] Li^+ ions are predominantly complexed with the EO groups.[8,28] We therefore assume that all Li^+ ions bind to the EO groups but are free to redistribute on the backbone.[29] As a first approximation, we ignore coordination of the Li^+ by multiple oxygen groups. The anions can be bound to the Li^+ on the PEO or it can be free. In our theory, the ion pair is treated as a charge-neutral species. The model is illustrated in Fig. 1. To describe the distribution of the Li^+ ions on the PEO backbone, we employ an Ising-like binding variable for the EO sites; $C_{is} = 1$ if there is a Li^+ ion at the s-th binding site of the i-th PEO chain, and 0 if there is not.[30] For the ion pair (EO–Li^+–X^-), we also need another binding variable; $D_{is} = 1$ if there is an EO–Li^+–X^-, and 0 if there is not.

The microscopic densities of the different species are given by

$$\hat{c}_+(\vec{r}) = \sum_i^{n_c} \sum_s^{N_A} C_{is}\delta\left(\vec{r} - \vec{R}_{is}^{A}\right)$$

$$\hat{c}_-(\vec{r}) = \sum_i^{n_- - n_{IP}} \delta\left(\vec{r} - \vec{r}_i^{(-)}\right)$$

$$\hat{c}_{IP}(\vec{r}) = \sum_i^{n_c} \sum_s^{N_A} C_{is}D_{is}\delta\left(\vec{r} - \vec{R}_{is}^{A}\right)$$

$$\hat{\phi}_p(\vec{r}) = v_p \sum_i^{n_c} \sum_s^{N_p} \delta\left(\vec{r} - \vec{R}_{is}^{p}\right)$$

$$\hat{\rho}_c(\vec{r}) = e\left[\hat{c}_+(\vec{r}) - \hat{c}_{IP}(\vec{r})\right] - e\hat{c}_-(\vec{r}). \quad (1)$$

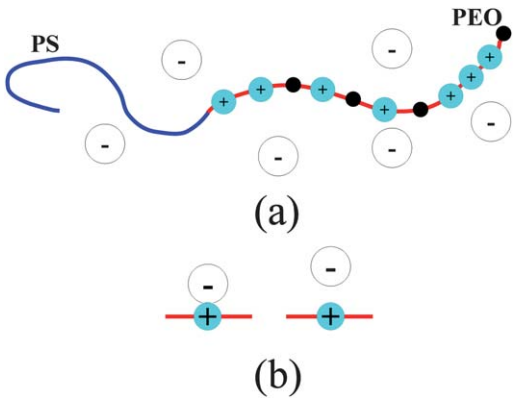

Fig. 1 Schematic description of a PEO-*b*-PS chain. The black filled circles denote binding sites of Li^+ ions, *i.e.*, EO monomers. (a) Li^+ ions are tightly bound to N_A binding sites of the PEO chain with the degree of polymerization N_A. The Li^+ ions are mobile on the PEO chain, so their distribution in the PEO is in general spatially inhomogeneous. (b) Binding and unbinding of an anion to EO–Li^+. The ion pair is described as a charge-neutral species.

$\hat{c}_+(\vec{r})$, $\hat{c}_-(\vec{r})$, and $\hat{c}_{IP}(\vec{r})$ are the number densities of the Li^+ ions, the free (unbound) anions, and the ion pairs. n_{IP} is the number of ion pairs given by $\int d\vec{r}\hat{c}_{IP}(\vec{r})$. $\hat{\phi}_p(\vec{r})$ is the volume fraction of polymer p (p = A, B), and $\hat{\rho}_c(\vec{r})$ is the charge density of the system. e is the elementary charge. $\vec{R}^p_{is}$, and $\vec{r}^{(-)}_i$ denote the position of the s-th monomer of the i-th polymer p, and the position of the i-th free anion, respectively. The number of the Li^+ ions at a local position $\vec{r}$ can be obtained by summing the binding variable C_{is}. Note that the number of Li^+ ions[10] on different polymer chains can be different, subject to the overall fixed number n_+ in the system, *i.e.*, C_{is} satisfies the condition,

$$\int d\vec{r}\,\hat{c}_+(\vec{r}) = \sum_i^{n_c}\sum_s^{N_A} C_{is} = n_+ \,. \tag{2}$$

The anions can either be bound with a EO–Li^+ in the form of an ion-pair, with a binding energy $-E_b$, or they can be free. A free anion interact differently with the different polymer components. To reflect this, we ascribe a composition dependent solvation energy. Although there may be non-electrostatic contributions in the solvation energy, these contributions are difficult to assess. Therefore, as a first step we take the solvation energy to be simply the Born energy of an ion. Taking kT as the unit of energy, the Born energy can be written as

$$V_{Born}(\vec{r}) = \frac{e^2}{8\pi a\varepsilon_0\varepsilon_r(\vec{r})} = \frac{l_0}{2a\varepsilon_r(\vec{r})}, \tag{3}$$

where a is the radius of the ion, ε_0 is electric permeability of vacuum, and $\varepsilon_r(\vec{r})$ is the local dielectric constant of the mixture.[25] We have introduced the vacuum Bjerrum length, $l_0 = e^2/(4\pi\varepsilon_0)$. In general, ε_r depends on the composition in some complicated manner. In this paper, we assume a simple volume-fraction-weighted average,

$$\varepsilon_r(\vec{r}) = \varepsilon_A\hat{\phi}_A(\vec{r}) + \varepsilon_B\hat{\phi}_B(\vec{r}). \tag{4}$$

The Born energy of all the free anions is

$$U_{Born} = \int d\vec{r}V_{Born}(\vec{r})\hat{c}_-(\vec{r}), \tag{5}$$

and the binding energy of anions to EO–Li^+ monomers is

$$U_{Bind} = -\int d\vec{r}\hat{c}_{IP}(\vec{r})E_b. \tag{6}$$

We do not explicitly consider the solvation energy of the Li^+ ion, as the primary solvation is by the oxygen groups, whose treatment will require quantum chemistry calculations. Its effects are accounted for phenomenologically through the ion-pair binding energy $-E_b$ and the monomer interaction parameters χ_1 and χ_2 introduced below.

Incidentally, using eqn (3), we estimate the free energy difference for a Li^+ ion between the PS and PEO domain to be about 44 kT, corresponding to a concentration ratio of 10^{-19}. This can be taken as another justification for assuming that all Li^+ ions are bound to the EO groups.

The block copolymers are assumed to be Gaussian chains, so the elastic energy of the polymers is written as

$$\mathcal{H}_0 = \sum_{i=1}^{n_c}\sum_{p=A,B}\sum_{s=1}^{N_p}\frac{3}{2b_p^2}\left(\vec{R}^p_{is} - \vec{R}^p_{is-1}\right)^2, \tag{7}$$

where b_p is the Kuhn length of polymer P. Here we have written the elastic energy in terms of the discrete Gaussian chain model because it is more natural to assign the binding variable introduced in eqn (2) to a discrete site. However, in calculating the chain propagators, we will turn to a continuous description of the Gaussian chain model.

Finally, the Coulomb interaction between the ions is given by

$$U_{ion-ion} = \frac{1}{2}\int d\vec{r}\,d\vec{r}\,'\hat{\rho}_c(\vec{r})v(\vec{r}-\vec{r}\,')\hat{\rho}_c(\vec{r}\,'), \tag{8}$$

where $v(\vec{r}-\vec{r}\,')$ is the Coulomb operator for a spatially varying dielectric medium, obtained from $-\nabla\cdot[\varepsilon_0\varepsilon_r(\vec{r})\nabla v(\vec{r})] = \delta(\vec{r})$.

The interaction between the EO and styrene monomers can be altered by the complexation of Li^+ ions on the EO and further binding of anions to the EO–Li^+ monomers. We therefore introduce the parameters χ_1 and χ_2 to reflect the shifts from the original χ due to the altered monomer identity in the EO–Li^+ and EO–Li^+–X^- monomers, respectively. The Flory–Huggins term representing the interaction between the A and B blocks now takes the form of

$$U_{FH} = \int d\vec{r}\left[\chi\hat{\phi}_A^{bare}(\vec{r}) + (\chi+\chi_1)\hat{\phi}_A^{EL}(\vec{r}) + (\chi+\chi_2)\hat{\phi}_A^{ELX}(\vec{r})\right]\hat{\phi}_B(\vec{r}), \tag{9}$$

where $\hat{\phi}_A^{bare}(\vec{r})$ and $\hat{\phi}_A^{EL}(\vec{r})$, and $\hat{\phi}_A^{ELX}(\vec{r})$ are the volume fractions of bare EO, EO–Li^+, and EO–Li^+–X^- monomers; the latter two can be related to the local concentration of Li^+ and the location fraction of ion pairs by stoichiometry:

$$\hat{\phi}_A^{EL}(\vec{r}) = \nu_A\left[\hat{c}_+(\vec{r}) - \hat{c}_{IP}(\vec{r})\right]$$

$$\hat{\phi}_A^{ELX}(\vec{r}) = \nu_A\hat{c}_{IP}(\vec{r}) \tag{10}$$

The Flory–Huggins part of the interaction energy now becomes,

$$U_{FH} = \int d\vec{r}\left[\chi\hat{\phi}_A(\vec{r}) + \chi_1\nu_A\left\{\hat{c}_+(\vec{r}) - \hat{c}_{IP}(\vec{r})\right\} + \chi_2\nu_A\hat{c}_{IP}(\vec{r})\right]\hat{\phi}_B(\vec{r}). \tag{11}$$

The total Hamiltonian of the system is the sum of the different energies discussed above, $\mathcal{H}_{tot} = \mathcal{H}_0 + U_{ion-ion} + U_{Born} + U_{Bind} + U_{FH}$, from which the partition function can be written as,

$$Z = \int \prod_{p=\mathrm{A,B}} \prod_{i}^{n_c} \prod_{s}^{N_A} \mathscr{D}C_{is}\mathscr{D}D_{is}\mathscr{D}\vec{R}_i^p(t) \prod_{k}^{n_- - n_{IP}} \mathrm{d}\vec{r}_k^{(-)} \times \frac{\xi_c^{n_c}\xi_-^{n_- - n_{IP}}}{n_c!(n_- - n_{IP})!} \times \delta\left[\vec{R}_i^A(N_A) - \vec{R}_i^B(0)\right] \times \prod_{\vec{r}} \delta\left[\sum_{\alpha=\mathrm{A,B}}^{+,-} \hat{\phi}_\alpha(\vec{r}) - 1\right] \times \delta\left[n_+ - \int \mathrm{d}\vec{r}\,\hat{c}_+(\vec{r})\right] \exp(-\mathscr{H}_{tot}). \quad (12)$$

ξ_c, and ξ_- are the internal partition function of the polymers and the free anions,[31] respectively. $\hat{\phi}_\alpha(\vec{r})$ is the volume fraction of all the species (α = A, B, +, and –). The functional integration over the binding variables C_{is} and D_{is} is a short hand notation for summing over these variables. The volume fractions of the ions are given by $\hat{\phi}_\pm(\vec{r}) = v_\pm\hat{c}_\pm(\vec{r})$. Since the Li^+ ions are small, and on account of possible electrostriction effect,[32] we ignore the volume of the Li^+ ion (*i.e.*, $v_+ = 0$). $\delta(\vec{R}_i^A(N_A) - \vec{R}_i^B(0))$ and $\delta(\sum_\alpha\hat{\phi}_\alpha(\vec{r}) - 1)$ enforces the connectivity between the two blocks and the incompressibility of the system. $\delta(n_+ - \int\mathrm{d}\vec{r}\hat{c}_+(\vec{r}))$ is a constraint for the total number of Li^+ ions in the system. The Li^+ ions are free to distribute among the binding sites of the different PEO chains, subject to this constraint and interactions with the anions.

The partition function in eqn (12) can be cast into a functional integration in terms of the density fields and their conjugate fields using standard techniques of the self-consistent field theory.[33] Details of the calculations are presented in Appendix A. The resulting free energy functional is

$$\begin{aligned} F = {} & \int \mathrm{d}\vec{r}\,\rho_0\eta\left[\sum_\alpha \phi_\alpha - 1\right] - n_c \ln\left[\frac{\xi_c V Q_c(\omega_p,\omega_+)}{n_c}\right] \\ & - n_c - (n_- - n_{IP})\ln\left[\frac{\xi_- V Q_-(\omega_-)}{(n_- - n_{IP})}\right] - (n_- - n_{IP}) \\ & + n_{IP}\ln\left[\frac{n_{IP}}{n_+}\right] + (n_+ - n_{IP})\ln\left[1 - \frac{n_{IP}}{n_+}\right] \\ & + \int \mathrm{d}^3r\left\{-\frac{\varepsilon_r}{8\pi l_0}|\nabla\psi|^2 + \psi[c_+(1-x) - c_-]\right\} \\ & - \sum_{p=\mathrm{A,B}}\int \mathrm{d}\vec{r}\,\rho_p\omega_p\phi_p - \sum_{\gamma=+,-}\int \mathrm{d}\vec{r}\,\omega_\gamma c_\gamma \\ & + \int \mathrm{d}\vec{r}\,V_{Born}c_- - \int \mathrm{d}\vec{r}\,x c_+ E_b \\ & + \int \mathrm{d}\vec{r}\,[\chi\phi_A + \chi_1 v_A c_+(1-x) + \chi_2 v_A x c_+]\phi_B \\ & + \mu\left[n_+ - \int \mathrm{d}\vec{r}\,c_+\right]. \end{aligned} \quad (13)$$

Here, $c_\gamma(\vec{r})$ is the density field of the ion, $\phi_p(\vec{r})$ is the volume-fraction field of polymer P, $x(\vec{r})$ is the order parameter for the fraction of Li^+ in ion pairs (see Appendix A), $\omega_\alpha(\vec{r})$ is a conjugate field of the species α, $\eta(\vec{r})$ is the incompressibility field, and $\psi(\vec{r})$ is the electrostatic potential. n_{IP} is now expressed as $\int\mathrm{d}\vec{r}x(\vec{r})c_+(\vec{r})$ (see Appendix A). μ is a chemical potential-like variable introduced to impose the constraint of the fixed total number of Li^+ ions. We have introduced the reference density, $\rho_0 = 1/v_0$, to make η dimensionless. Q_c, and Q_- are the configuration partition functions of a single-chain block copolymer and an anion (given in Appendix A), respectively. The appearance of the field ω_+ in Q_c is a result of summing over the Ising-like binding variable, which couples ω_+ to ω_A.† We also show the explicit form of the mean-field equations for the field variables in eqn (A7).

For determining the order–disorder transition and the spinodal of the disordered phase, it is useful to first obtain the solution of the SCF equations for the uniform disordered phase by extremizing the free energy functional $F(\Omega)$ with respect to the field variables Ω. Denoting the spatially uniform solutions with an over bar, we have:

$$\begin{aligned} \phi_p(\vec{r}) &= \overline{\phi}_p, \\ c_\gamma(\vec{r}) &= c_0, \\ \omega_\alpha(\vec{r}) &= \overline{\omega}_\alpha, \\ \psi(\vec{r}) &= \overline{\psi} \\ x(\vec{r}) &= x \end{aligned} \quad (14)$$

where c_0 is the overall salt concentration in the system. Neglecting the inconsequential linear terms in the densities, the free energy density of the homogeneous phase can be written in the form,

$$\begin{aligned} \frac{F^{(0)}}{V} = {} & f_{id} + f_{anion}(c_0, x, \overline{\phi}_A) \\ & + [\chi + \chi_1 r(1-x) + \chi_2 r x]\overline{\phi}_A\overline{\phi}_B, \end{aligned} \quad (15)$$

where f_{id} is the translational entropy of the noninteracting ideal block copolymer chains, and

$$\begin{aligned} f_{anion}(c_0, x, \overline{\phi}_A) = {} & \frac{r\overline{\phi}_A}{v_A}\left[x\ln x + 2(1-x)\ln(1-x) - (1-x)\right. \\ & \left. + (1-x)\ln\left(\frac{r\overline{\phi}_A}{v_A\xi_-}\right) - xE_b + (1-x)V_{Born}\right] \end{aligned} \quad (16)$$

includes the solvation free energy and translational entropy of the free anions, the free energy of bound anions, as well as binding energy due to ion-pairing. $r = \frac{v_A c_0}{\overline{\phi}_A}$ is the commonly used definition for salt loading, *i.e.*, the molar ratio of Li^+ to the EO

† In the case of $x(\vec{r}) = 0$, the free energy functional reduces to the one for no ion pair, whose form may appear different from the one in ref. 23. However, these two equations are completely equivalent. For conciseness, in ref. 23, we absorbed the chemical potential-like variable μ into the definition of ω_+, and made use of the incompressibility directly instead of introducing the incompressibility field to enforce it. In the present work, we keep these auxiliary variables for the mathematical convenience. In ref. 23, we also absorbed the volume factor into the definition of the partition functions Q_c, and Q_- and dropped the inconsequential momentum partition functions ξ_c and ξ_-.

monomers. We note that eqn (15) can be obtained by a simple thermodynamic argument and has a similar form to the free energy for the case of a salt-doped binary polymer blend.[23]

Minimizing the free energy eqn (15) with respect to x leads to the ion pair equilibrium condition,

$$\frac{x}{(1-x)^2} = \left(\frac{\alpha r \overline{\phi}_A}{v_A}\right)\exp(V_{Born}), \tag{17}$$

with

$$\alpha = \frac{\exp[E_b + (\chi_1 - \chi_2)v_A\overline{\phi}_B]}{\xi_-}. \tag{18}$$

The right-hand side of eqn (17) can be considered as the binding constant for the formation of the EO–Li^+–X^- ion pair, where we have separated out the bare binding constant α from the energetic effect of the Born energy of the anion. In ref. 23, we showed that the nonlinear dependence of the ion-pair fraction x on the salt loading r results in a nonlinear dependence of χ_{eff} on r. This result allows us to estimate an upper limit for α from the measured the measured dependence of χ_{eff} on r. In the case of PEO-PS melt containing LiTFSI, very good linearity for χ_{eff} with r was observed[20] from which we estimated α_{limit} at $\sim 5 \times 10^{-6}$ [M^{-1}],[23] corresponding to a ion-pair fraction $x < 7\%$. Such a small fraction has insignificant consequences on the thermodynamics of the salt-doped block copolymers. We will henceforth neglect ion-pair formation in the rest of this paper and so the parameter χ_2 becomes irrelevant.

If we accept the Born solvation model together with the mixing rule for the dielectric constant, our theory has only one adjustable parameter χ_1. A first-principles determination of this parameter would require quantum chemistry calculations. Alternatively, as shown in ref. 23, χ_1 can be obtained from fitting the experimentally measured dependence of χ_{eff} on the anion radius to our predicted result.

III. Structure factor in the disordered phase

In this section, we study the effect of adding lithium salts on the stability of the disordered phases by calculating the structure factor for the diblock copolymers. The shift in the spinodal of can then be used to define an χ_{eff} between the two blocks. As explained in the model setup, we consider a completely symmetric diblock copolymer, with the following choice of parameters: $v_A = v_B = v_0 = 0.1$ nm^3, $f_c = 0.5$, $b_A = b_B = b = 0.56$ nm, $l_0 = 43.6$ nm, $\varepsilon_A = 7.5$, $v_0\chi = 0.1$. To examine the effects of the Born energy, we allow ε_B to have two different values 4.0 and 7.5, the latter as a comparison. Also, to focus on the electrostatic and solvation effects, we set $v_0\chi_1 = 0$.

The structure factor is calculated at the level of the random phase approximation, which is tantamount to an expansion of the free energy around the homogeneous phase to quadratic order in the field variables. The partition function (eqn (12)) to this order can then be approximated as

$$Z \approx \exp\left(-F^{(0)}\right)\int \mathcal{D}\Omega\ \exp\left(-\Delta F^{(2)}\right), \tag{19}$$

where Ω symbolically denotes all the field variables and the absence of the first-order contribution reflects the stationary (saddle-point) nature of the free energy at the homogeneous state.

We first write the field variables in terms of deviation from their values in the homogeneous state,

$$\phi_p(\vec{r}) = \overline{\phi} + \delta\phi_p(\vec{r})$$

$$c_\gamma(\vec{r}) = c_0 + \delta c_\gamma(\vec{r})$$

$$\omega_\alpha(\vec{r}) = \overline{\omega}_\alpha + \delta\omega_\alpha(\vec{r})$$

$$\psi(\vec{r}) = \overline{\psi} + \delta\psi(\vec{r}), \tag{20}$$

Without loss of generality, we may set the bulk values of the conjugate fields and electrostatic potential as $\overline{\omega} = 0$ and $\overline{\psi} = 0$. Although there is no difficulty in accounting for the volume of ions (we will consider the volume of the anions for the lamellar phase in Section IV C and V), for simplicity we consider low salt concentration and treat the ions as volumeless particles in this section, that is, $v_+ = v_- = 0$. The incompressibility condition is then given by $\phi_A(\vec{r}) + \phi_B(\vec{r}) = 1$, or $\delta\phi_A(\vec{r}) + \delta\phi_B(\vec{r}) = 0$. We then obtain[34,35] (see Appendix B)

$$\begin{aligned}\Delta F^{(2)} = {} & \Delta F_0^{(2)}\left(\delta\omega_p^{eff}, \delta\phi_A\right) + \Delta F_{Born}^{(2)}(\delta c_-, \delta\phi_A) \\ & + \Delta F_{ion-ion}^{(2)}(\delta\psi, \delta c_\gamma, \delta\omega_\gamma, \delta\phi_A) \\ & + \Delta F_{\chi-shift}^{(2)}(\delta c_+, \delta\phi_A)\end{aligned} \tag{21}$$

where $\Delta F_0^{(2)}$, $\Delta F_{Born}^{(2)}$, $\Delta F_{ion-ion}^{(2)}$, and $\Delta F_{\chi-shift}^{(2)}$ denote the free energies for the salt-free system, the Born energy contribution, the ion–ion interaction, and the shift in χ due to the EO–Li^+ complexation, respectively. For nonzero χ_1 and χ_2, the last term also includes effects due to these parameters; see eqn (13). Here, $\Delta F_{Born}^{(2)}$ is a function of $(\varepsilon_A - \varepsilon_B)$, so the effect of the Born energy vanishes when the dielectric constants of the two blocks are the same.

Next, we integrate over all field variables other than $\delta\phi_A(\vec{r})$ in eqn (19). Since the integrand is Gaussian, the integration is equivalent to extremizing eqn (21) with respect to these field

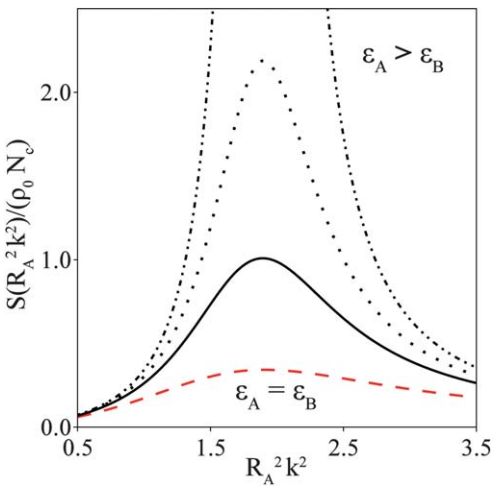

Fig. 2 Scattering function $S(R_A^2k^2)/\rho_0 N_c$. $N_c = 100$, $b_A = b_B = 0.56$ nm, $v_A = v_B = v_0 = 0.1$ nm^3, $v_0\chi = 0.1$, $v_0\chi_1 = 0.0$, $f_c = 0.5$, $l_0 = 43.6$ nm, and $a = 0.38$ nm. The salt concentrations are $c_0 = 0$ nm^{-3} (solid line), $c_0 = 2 \times 10^{-3}$ nm^{-3} (dotted line), and $c_0 = 3.7 \times 10^{-3}$ nm^{-3} (dot-dashed line). For these lines, $\varepsilon_A = 7.5$ and $\varepsilon_B = 4.0$. The red dashed line corresponds to the case of no preferential solvation energy, $\varepsilon_A = \varepsilon_B = 7.5$, with $c_0 = 2 \times 10^{-3}$ nm^{-3}.

variables (Appendix B).[35] In Fourier space, we obtain the following effective quadratic free energy function $\Delta F_{\mathrm{eff}}^{(2)}$

$$\Delta F_{\mathrm{eff}}^{(2)} = \frac{1}{2}\int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\delta\phi_{\mathrm{A}}(\vec{k})S^{-1}(\vec{k})\delta\phi_{\mathrm{A}}(-\vec{k}). \qquad (22)$$

The inverse of the structure factor, $S^{-1}(\vec{k})$, is given by S_0^{-1} + S_{ions}^{-1} where S_0^{-1} is that for the salt-free system (36) and S_{ions}^{-1} contains the coupled effects of all the interactions associated with the ions. In Fig. 2, we show the structure factor as a function of $R_{\mathrm{A}}^2k^2$, where $R_{\mathrm{A}}^2 = N_{\mathrm{A}}b_{\mathrm{A}}^2/6$ is the mean-square radius of gyration for block A (PEO). As in the case of salt-free diblock copolymers, $S(R_{\mathrm{A}}^2k^2)$ peaks at some finite wavenumber k^*, corresponding to the size of the microphase separated domains. For comparison, we first consider the case of equal dielectric constant for both blocks; in that case, the Born energy effect vanishes, leaving only the Coulomb interaction between the ions and the translational entropy of the anions. For this case, the peak value of $S(R_{\mathrm{A}}^2k^2)$ at k^* decreases upon the addition of salt, relative to the salt-free system, indicating enhanced miscibility between the two blocks, just as for ordinary charged block copolymers.[37,38] As we have argued in ref. 23, without the solvation energy effect, the translational entropy of the anions always makes the two components more miscible because phase separation incurs an entropic cost for the counterions due to electroneutrality.

We now consider the effect of the Born energy for the case of interest with $\varepsilon_{\mathrm{A}} > \varepsilon_{\mathrm{B}}$. In this case, the peak value of $S(R_{\mathrm{A}}^2k^2)$ increases with salt concentration c_0 and diverges when c_0 exceeds a critical value, which defines the spinodal of the disordered phase. In fact, even if the intrinsic interaction between the two blocks is zero, *i.e.*, $\chi = 0$, microphase separation can be induced simply by adding salts. This enhanced unfavorable interaction between the higher-dielectric and lower-dielectric blocks is due to the tendency of the anions to be preferentially solvated by the higher-dielectric component, which overcomes the translational entropy of the anions and provides a driving force for phase separation. In the presence of added salts, the value of χ at the spinodal, χ^*, is shifted from its value for the salt-free systems. This shift can be considered as the net contribution due to the salts to an effective χ, thus defining a χ_{eff}. Our theory predicts[23] a linear increase in χ_{eff} as a function of the salt loading r, with larger slopes for smaller anion sizes, in agreement with experiments.[17,20] In order to get a sense of the relative contribution due to the Born energy to other contributions, we note that in ref. 38 it was shown that the Coulomb interactions and translational entropy of the ions make comparable contributions to the effective interaction between the two blocks. Furthermore, in ref. 23, we provided a simple expression for the change in the effective χ_{eff} parameter for a binary polymer blend, showing the separate contributions due to the Born energy and the translational entropy of the anions. While χ_{eff} for the diblock copolymer differs quantitatively from that for the binary blend, they are of comparable order of magnitude and have similar behavior.[23] Using the expression for the polymer blend, we estimate the effects due to the Born energy to be roughly an order of magnitude larger than the contributions from the translational entropy of the anions and the Coulomb interactions.

Unlike the salt-free systems for which k^* is independent of the interaction parameter χ, there is a noticeable shift in k^* with temperature and salt concentration; in general, k^* decreases with increasing temperature and increases with increasing salt concentration (Fig. 3). Because the salt ion is volumeless in our calculations, this shift in k^* is clearly a result of the effects of the Born energy. We note that while one experimental study[15] seems to confirm this effect, other experimental results appear to show the opposite behavior.[14,21] We believe the apparent contradiction in the dependence on salt concentration is due to the counteracting effects of the volume of the ions in the experiments, which can mask the rather moderate effects shown in Fig. 3(b). Similarly, the discrepancy between the temperature dependence shown in Fig. 3(a) and experimental results can be explained by considering effects such as the temperature dependence of the Kuhn length b_p, which is not included in our model. On physical grounds, the Kuhn length should decrease with increasing temperature, leading to a decrease in the end-to-end distance of polymer and hence increase in k^*. The shift in k^* in Fig. 3(a) can thus be counteracted by this effect.

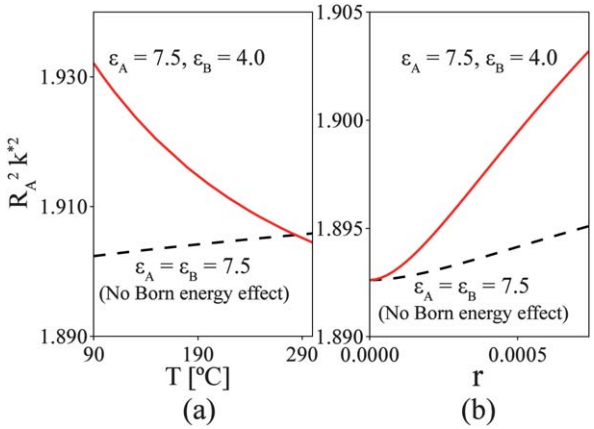

Fig. 3 The peak position of $S(R_{\mathrm{A}}^2k^2)$ as a function of the temperature T and salt loading r in the disordered phase. The dashed line corresponds to the case of no preferential solvation energy. $N_{\mathrm{c}} = 100$, $b_{\mathrm{A}} = b_{\mathrm{B}} = 0.56$ nm, $v_{\mathrm{A}} = v_{\mathrm{B}} = v_0 = 0.1$ nm^3, $v_0\chi_1 = 0.0$, $f_{\mathrm{c}} = 0.5$, and $a = 0.38$ nm. (a) $r = 0.006$ and $v_0\chi = -0.00705 + 21.3/T$ (ref. 39) (b) $v_0\chi = 0.1$ and $l_0 = 43.6$ nm.

IV. The lamellar phase

We now consider the lamellar phase of the salt-doped diblock copolymer, focusing on the ion distribution, the domain spacing and the relationship between the χ_{eff} obtained from the structure factor in the disordered phase and an effective χ obtained from the domain spacing. The model parameters are the same as in Section III, *i.e.*, $v_{\mathrm{A}} = v_{\mathrm{B}} = v_0 = 0.1$ nm^3, $f_{\mathrm{c}} = 0.5$, $b_{\mathrm{A}} = b_{\mathrm{B}} \equiv b =$ 0.56 nm, $l_0 = 43.6$ nm, $\varepsilon_{\mathrm{A}} = 7.5$, $v_0\chi = 0.1$, and $v_0\chi_1 = 0.0$. However, to address the effectiveness of the incompressibility field on the ion distribution, we ascribe a volume to the anion, $v_- = 1$ nm^3. To examine the effects of the Born energy, we again vary ε_{B}.

For the lamellar structure, the SCFT equations are one-dimensional with periodic boundary conditions. We employ the Crank–Nicolson method to solve the diffusion equation for the chain propagator and the fourth-order Runge–Kutta method to solve the Poisson–Boltzmann equation. The free energy is calculated for different values of the domain spacing D/b; the

equilibrium is determined by the minimum of the free energy, taking the step of $\Delta(D/b) = 0.5$. The lattice grids of the spatial interval [0, D/b], and the space-curve for the chain [0, N_c] are set to 200, and 400, respectively. The condition for the self-consistency is set to max $|\omega_i^{new}(\vec{r}) - \omega_i^{old}(\vec{r})|$ and max $|\psi_i^{new}(\vec{r}) - \psi_i^{old}(\vec{r})| \lesssim 10^{-7}$ in the computation of the self-consistent equations. For good convergence, a scheme to push the potentials towards the incompressibility condition developed by Shi and Noolandi[40] is used.

A. Ion distribution and electrostatic potential

While the cation is bound to the backbone of block A (PEO), the anions are free to distribute, subject to the electrostatic interaction with the cations and the solvation energy. To highlight the effect of the anion solvation energy, we consider two cases by varying the dielectric constant of block B (PS). In the first case, we set $\varepsilon_B = 4.0 < \varepsilon_A = 7.5$, and in the second case, we have $\varepsilon_B = \varepsilon_A = 7.5$; all other parameters are kept the same. Because of the preferential solvation energy in the first case, the two blocks are strongly segregated in the first case, with very low ion concentration in the B-rich domain; see Fig. 4(a). The figure also shows clear charge separation at the A/B interface, with accumulation of negative charge on the A-side and positive charge on the B-side. This polarization of the interface correlates with the electrostatic potential shown in Fig. 4(b).

For the second case with equal dielectric constant for the two blocks, there is no energetic difference for the anion to be solvated by either block. Thus the driving force for segregation of the two blocks due to anion solvation disappears and the two blocks are segregated to a lesser degree. Because of the Coulomb attraction by the cations, the concentration of anions is still higher in the A-rich domain, but there is significant ion concentration for both types in the B-rich domain; see Fig. 4(d). Interestingly, the surface polarization has an opposite sign to the first case, with the positive charge accumulation now on the A-side and negative accumulation on the B-side. This polarization corresponds to an electrostatic potential profile shown in Fig. 4(e), whose shape is opposite to that in the first case [Fig. 4(b)]. As the electrostatic potential is part of the potential field for the motion of the ions, these results can have consequences for ion transport.

B. Annealed *vs.* fixed charges on the PEO

A key difference between the Li^+-complexed PEO (ignoring multiple coordination of Li^+ by the O groups) and ordinary polyelectrolytes is that the charges are fixed on the backbone in the latter but can redistribute in the former. This effectively makes the Li^+-complexed PEO a polyelectrolyte with annealed charge distribution that can respond to the local environment. This difference has significant effects on the resulting spatial distribution for both cations and anions. To illustrate, in Fig. 5 we show the concentration of the Li^+ ions for both the annealed (solid line) and fixed, uniform distribution on the backbone of block A (PEO). For the fixed charges, uniform charge distribution on the

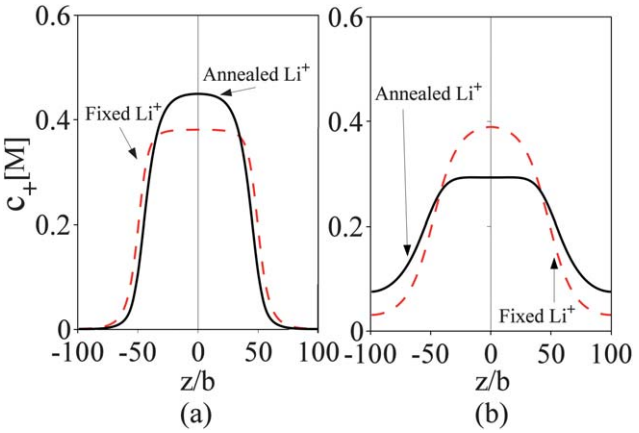

Fig. 5 Spatial distribution of Li^+ ions. $N_c = 200$, $c_0 = 0.2$ [M], and $a = 0.24$ nm. The solid and dashed lines correspond, respectively, to the annealed and fixed ions distribution on the PEO backbone. (a) $\varepsilon_B = 4.0$. (b) $\varepsilon_A = \varepsilon_B = 7.5$ (no Born energy effect).

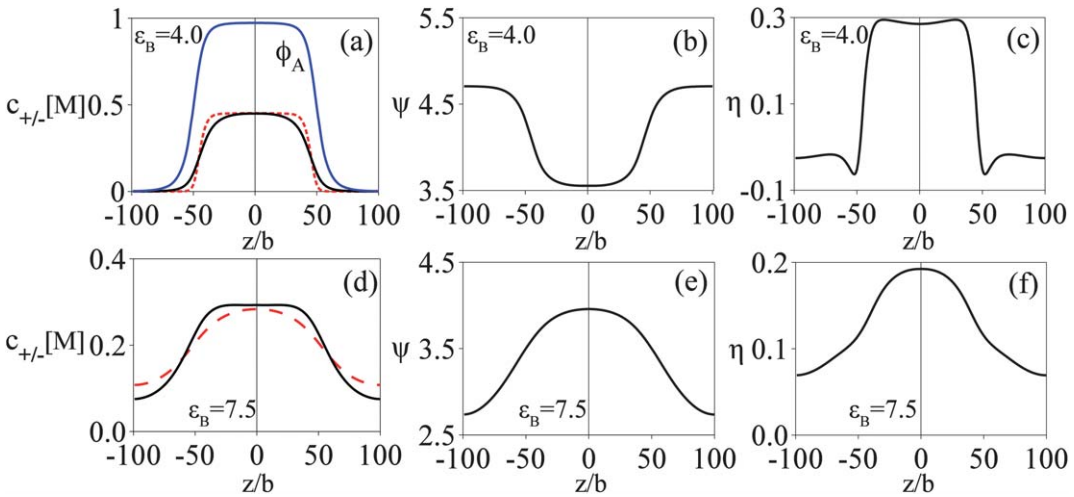

Fig. 4 Concentration and field profiles in the lamellar phase. $N_c = 200$, $c_0 = 0.2$ [M], and $a = 0.24$ nm. $\varepsilon_B = 4.0$, and $\varepsilon_B = 7.5$ (no Born energy effect) for (a)–(c), and (d)–(f), respectively. (a) and (d) The volume fraction of higher dielectric polymer A (blue solid line), the Li^+ concentration (black solid line), and the anion concentration (red dashed line). (b) and (e) The electrostatic potential. (c) and (f) The incompressibility field.

backbone of block A results in $c_+(\vec{r}) = r\phi_A(\vec{r})/v_A$ (dashed lines). Because the anions are primarily present in the A-rich phase due to the preferential solvation energy, the attraction by the anions through the electrostatic interaction leads to an enhanced distribution of the Li^+ ions in the annealed case, relative to fixed charges; see Fig. 5(a). When there is no preferential solvation energy ($\varepsilon_B = \varepsilon_A = 7.5$), the opposite trend is observed, where the Li^+ ions are pushed toward the B-rich domain; see Fig. 5(b). In the absence of the preferential solvation energy for the anions, their concentration in the B-rich domain tends to increase due to translational entropy. The Li^+ ions are then dragged into the B-rich phase by the anions through the electrostatic attraction.

C. Local incompressibility field

As mentioned in the introduction, Gomez *et al.*[11] observed an increased localization of the Li^+ ions towards the center of the PEO domain in the lamellar phase as the molecular weight of the block copolymer is increased at fixed block ratio. These authors conjectured that this result arises from spatial distribution of the local stress field of the ordered structures,[24] which was calculated from $(d\vec{R}_i^p(t)/dt)^2$ for the salt-free system. We have also examined the ion distribution for several molecular weights of the block copolymer and do not observe the localization effect. The explanation of this localization effect probably lies in factors not considered in our current work, such as the image force on the ions and the multiple coordination of the Li^+ by several EO groups. However, our theory still provides useful insight on the factors affecting the ion distribution. Instead of the Li^+ distribution, for which there is not a simple analytical expression, we examine the anion distribution, which is strongly correlated to the Li^+ distribution due to the electrostatic interaction. Within the self-consistent field approximation, it is straightforward to show that the ratio of the anion concentrations at $\vec{r}_1$ and $\vec{r}_2$ is then given by (Appendix A)

$$\frac{c_-(\vec{r}_1)}{c_-(\vec{r}_2)} = e^{\Delta\psi - v_-\Delta\eta - \Delta V_{\mathrm{Born}}}, \tag{23}$$

where Δ denotes the difference between the variables at $\vec{r}_1$ and $\vec{r}_2$. This result shows that the distribution of the anions is determined by three factors, the local electrostatic potential $\psi(\vec{r})$, the local incompressibility field $\eta(\vec{r})$ and the location solvation energy $V_{\mathrm{Born}}(\vec{r})$. For salt-free block copolymers, we find that the local incompressibility field follows a similar profile to the local stress field in ref. 24 and thus we use the local incompressibility field as a substitute for the local stress field in discussing the effects of the latter. Eqn (23) shows that anions will accumulate where this field is small or negative and the effect depends on the anion volume. Thus, based on Fig. 4(c) and (f), if the ion distribution is determined by the incompressibility field alone, we would expect the highest concentration at the PS domain or at the interface. This is clearly not the case and suggests the importance of the other two factors. Furthermore, the addition of salts into the block copolymers leads to qualitative changes in the incompressibility field profile—the field has a deep minimum at, and a mirror symmetry with respect to, the A–B interface for the salt-free block copolymers, which is drastically different from the profiles shown in Fig. 4(c) and (f).

Therefore, while we have not explained the observed localization of the Li^+ ion distribution in the PEO domain, our study shows that the local stress field of the salt-free system does not provide useful correlation for this effect because, firstly, the field can be qualitatively altered by the addition of salt and secondly, effects due to the electrostatic potential and local solvation energy are equally if not more important.

D. Domain spacing

Increase in the domain spacing upon lithium salt loading is one of the key findings in experiments.[17,18,21] Note that this increase is beyond the simple increase in the volume of the domain due to the addition of the lithium salt and therefore must reflect changes in the thermodynamics of the block copolymer upon adding the salt. Fig. 6 shows the increase in the domain spacing as a function of salt loading for $\varepsilon_A = 7.5$, $\varepsilon_B = 4.0$ for several values of the anion radii. The effect is stronger for smaller anions, consistent with the role of the solvation energy for the anions. The tendency for the anions to be preferentially solvated by block A results in an effective repulsion between the two blocks, which in turn leads to increased domain spacing. For comparison, we consider the case of no preferential solvation energy for the anions by setting $\varepsilon_A = \varepsilon_B = 7.5$. In this case, the domain spacing *decreases* with increasing salt concentration. As mentioned in Section I and III, in the absence of the preferential solvation energy for the anions, their translational entropy leads to enhanced miscibility between the two blocks,[37,38,41] which correlates with decreased domain spacing. However, as we have shown in Section III, the addition of salts not only gives rise to an effective χ_{eff}, but also leads to a shift in the peak position of the structure factor in the disordered phase. For $\varepsilon_A > \varepsilon_B$, adding salts leads to a shift towards larger wave number. Thus the increase in the domain spacing with salt concentration is not simply a reflection of the increase in χ_{eff}. This point is discussed further in the next subsection.

E. Different definitions of χ_{eff}

The domain spacing of microphase separated salt-free block copolymers in the intermediate to strong segregation regimes is known to be described by the scaling relation, $D \sim \chi^{\nu}$, where the

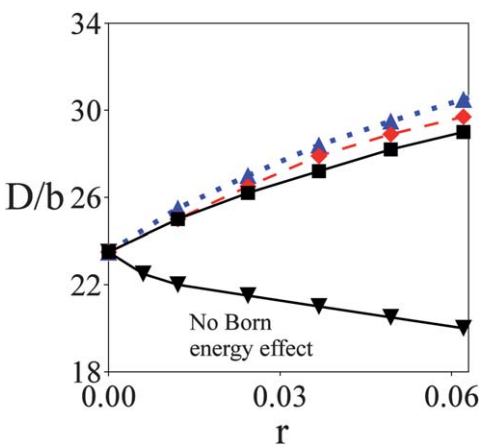

Fig. 6 Domain spacing D/b as a function of the salt loading r. $\varepsilon_A = 7.5$, $\varepsilon_B = 4.0$ for the upper three lines with $a = 0.38$ nm (black squares), $a = 0.315$ nm(red diamonds), and $a = 0.24$ nm (blue triangles). Inverted triangles for $\varepsilon_A = \varepsilon_B = 7.5$ correspond to the case of no preferential solvation energy.

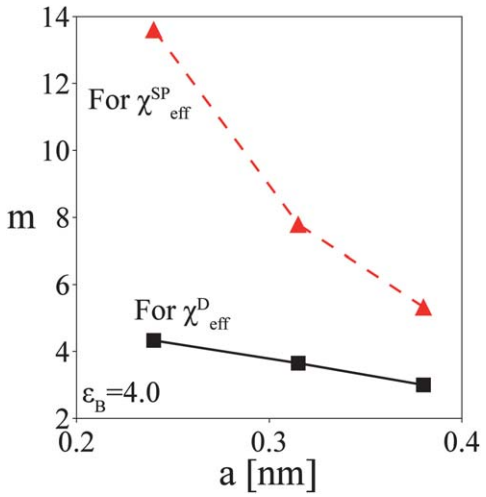

Fig. 7 The slope m (defined from the linear dependence of χ_{eff} on r, *i.e.*, $\chi_{eff} = \chi + mr$), for different radii of anions a. The radii of anions are a = 0.240, 0.315, and 0.380 nm. The solid squares, and triangles show m calculated by the domain spacing D, and the spinodal, respectively. The lines are a guide for the eye.

exponent υ ranges from 1/6 to 1/3, depending on the degree of segregation.[42] Such a scaling relation was used by Epps and co-workers for defining a χ_{eff} based on experimentally measured domain spacing[17,18] *via* $D_{doped}/D_{undoped} = (\chi^{D}_{eff}/\chi)^{\upsilon}$ with $\upsilon = 1/6$ (Fig. 7), where D_{doped}, and $D_{undoped}$ are the domain spacings for the salt-doped and salt-free systems, respectively. We use the superscript D in χ^{D}_{eff} denote this particular definition based on the domain spacing. Using the same scaling relationship but with a slightly different scaling exponent of $\upsilon = 1/5$ (determined from best fitting), we have obtained χ^{D}_{eff} as a function of the salt loading for different anion radii and dielectric contrast between the two blocks. As in the work of Epps and Young,[17,18] we found a good linear relationship between χ^{D}_{eff} and the salt concentration r. Therefore, we characterize the behavior of χ^{D}_{eff} by the slope of this linear relationship, m. In Fig. 7, we show the dependence of m on the anion radius for $\varepsilon_A = 7.5$, $\varepsilon_B = 4.0$. Shown in the same figure is m for χ^{D}_{eff}, the effective χ determined from the shift in the spinodal of the disordered phase. While m obtained from both definitions behave qualitatively similar with the anion radius, m for χ^{sp}_{eff} is clearly larger than m for χ^{D}_{eff}, implying $\chi^{sp}_{eff} > \chi^{D}_{eff}$.

To understand the difference between χ^{sp}_{eff} and χ^{D}_{eff}, recall that the addition of the lithium salt to block copolymers with dielectric contrast affects both the height and location of the peak of the structure factor of the disordered phase—the peak height increases, and the location shifts to *larger* wavenumber, suggesting a decreased characteristic length scale for microphase separation. Therefore, while for the salt-free block copolymers the increase in the domain spacing is due purely to the increase in the effective repulsion between the two blocks, for the salt-doped system, the increase of the domain spacing with salt loading reflects the combined effects due to both the increased effective repulsion between the two blocks and a decrease in the length scale for microphase separation. The χ^{D}_{eff} obtained from the domain spacing thus has contributions from these two opposing effects. Therefore, $\chi^{sp}_{eff} > \chi^{D}_{eff}$. Because χ^{sp}_{eff} is more closely related to the change in the thermodynamic driving force for microphase separation, whereas χ^{D}_{eff} has the additional (opposing) effects of the shrinkage in the domain spacing, we thus propose that χ^{sp}_{eff} is a better and more fundamental measure of the change in the effective repulsion between the two blocks. Recently, Epps and Young *et al.* found that χ^{D}_{eff} obtained from the domain spacing of the cylinder phase is different from that obtained the domain spacing of the lamellar phase.[17,18] This observation suggests that χ^{D}_{eff} is not a consistent measure of effective repulsion between the two blocks, thus lending support to our proposal.

Another definition of χ_{eff} was used in ref. 20 and 21, using the shift in the phase boundaries. Our work has not studied ordered phases other than the lamellar phase, so we are unable to directly address the soundness of the effective χ obtained from the shift in the phase boundaries, χ^{pb}_{eff}. For the transition between the disordered phase and the lamellar phase, the spinodal coincide with the order–disorder-transition, so we suspect that χ^{pb}_{eff} is probably close to χ^{sp}_{eff}. We will address this issue in future work.

V. Discussion and conclusion

In this work, we have developed a self-consistent field theory for ion-containing diblock copolymers, taking polyethylene oxide (PEO), polystyrene and lithium salts as an example. Our theory accounts for the annealed distribution of Li^+ ions bound to the PEO, the translational entropy of the counterions (anions), the preferential solvation energy of the anions in the PEO domain, and the ion-pair equilibrium between EO-complexed Li^+ and anion. Several issues of experimental relevance are studied including the shift in the order–disorder transition temperature (which coincide with the spinodal of the disordered phase for transition to the lamellar phase at the level of mean-field theory[36,43]), domain spacing, and ion distribution in the ordered lamellae, upon salt loading. A key effect in this system is the preferential solvation energy of the anions, which provides a driving force for microphase separation of the two blocks, counteracting the tendency for increased miscibility due to the translational entropy of anions. The latter effect has been well-known in polyelectrolyte systems,[37,38,41] whereas immiscibility induced by the solvation energy of salt ions is a new feature for the ion-containing polymers. Furthermore, our theory predicts that, unlike the salt-free system, the peak position of the structure factor of the disordered phase decreases with temperature and increases with salt loading; these shifts are consistent with an earlier observation in the experiment by Ruzette *et al.*[15]

An issue of particular interest is the definition of an effective χ parameter to characterize the increased tendency for microphase separation of the two blocks upon salt doping. Experimentally, χ_{eff} has been identified by the changes in the structure factor of the disordered phase,[14] by the shift in the phase boundaries,[20,21] and by the change in the domain spacing of the ordered phases.[17,18] Within the framework of mean-field theory, our work shows that an unambiguous definition is through the shift in the spinodal of the disordered phase. We argue that this effective χ, which we denote by χ^{sp}_{eff} is the most fundamental measure of the increased effective repulsion between the two blocks due to salt doping. The effective χ obtained from the domain spacing of the ordered phases through the use of the scaling relation between the χ-parameter and the domain spacing for salt-free block copolymers, which we denote as χ^{D}_{eff}, has effects in addition to

change in the thermodynamic driving force for microphase separation, and is shown to be always less than χ^{sp}_{eff}.

We close by making some general remarks about the solvation energy of ions. Solvation of ions has always been an important area of research in chemistry.[32] However, in the polyelectrolyte and soft matter literature, the effects of ion solvation have been largely ignored. Here we have shown that the preferential solvation energy of the anions produces qualitatively new effects on the structure and phase behavior in salt-doped block copolymers. In general, the effects of preferential ion solvation must be considered whenever one studies systems involving phase separation or spatial inhomogeneity. In this work, we have used a very crude expression of the solvation energy in the form of the local Born model based on continuum dielectrics with a crude mixing rule of the dielectric constant for the mixture. In this approximation, the preferential solvation energy is reflected through the contrast in the dielectric constant of the component. While this crude approximation captures the qualitative features of the effects of preferential solvation of the anions, a more accurate expression can be obtained by explicitly accounting for the polarizability and permanent dipoles of the solvating molecules.[44,45]

Appendix A: derivation of the mean-field equations

In this Appendix, we show the derivation of the self-consistent field equations. To obtain the free energy functional of the system, we introduce the coarse-grained volume fraction field $\phi_\alpha(\vec{r})$ for the polymers *via* the constraint

$$\delta\left[\hat{\phi}_\alpha(\vec{r}) - \phi_\alpha(\vec{r})\right] = \int \mathcal{D}\omega \exp\left\{ i \int d\vec{r}\omega_\alpha(\vec{r}) \times \left[\hat{\phi}_\alpha(\vec{r}) - \phi_\alpha(\vec{r})\right] \right\}. \tag{A1}$$

in the partition function and performing the integration over $\phi_\alpha(\vec{r})$. $\omega_\alpha(\vec{r})$ is a conjugate field introduced through the Fourier representation of the δ-function. A similar procedure is performed for the concentration of the ions. In addition, we expect the average number density of ion pairs to be in the form of xc_+ with x being the fraction of Li^+ in ion pairs, and c_+ the total concentration Li^+ ions. Therefore, we also perform a coarse-graining of the number density of the ion pairs $\hat{c}_{IP}$ by inserting the constraint $\delta[\hat{c}_{IP}(\vec{r})/c_+(\vec{r}) - x(\vec{r})]$ into the partition function and performing the functional integration over x. This x serves as an order parameter, and hence the final form of the free energy will be minimized with respect to $x(\vec{r})$.

Carrying out the summation for the binding variable, C_{is} with $C_{is} = 1$ for Li^+-complexed EO monomers and $C_{is} = 0$ for empty EO monomers, and the similar variable D_{is} for the ion pair [this leads to the binomial coefficient ${}_{n_+}C_{nIP}$ in the partition function, eqn (12), and the entropy term for the Li^+ ions in the third line of eqn (13)], and performing the integration over the conformation of the polymers, the partition function, eqn (12) can be cast into a functional integral of the general form,

$$Z = \int \mathcal{D}\Omega \ \exp[-F(\Omega)]$$
$$\mathcal{D}\Omega \equiv \prod_{p=A,B} \prod_{\gamma=+,-} \mathcal{D}\phi_p \mathcal{D}c_\gamma \mathcal{D}x \mathcal{D}\omega_p \mathcal{D}\omega_\gamma \mathcal{D}\psi \mathcal{D}\mu \mathcal{D}\eta. \tag{A2}$$

The free energy functional of the system $F(\Omega)$ is given by eqn (13), in which the partition functions for the chain and anion are respectively

$$Q_c = \frac{1}{V}\int \mathcal{D}\vec{R}(t)\delta[\vec{R}^A(N_A) - \vec{R}^B(0)] \times \exp\left(- \sum_{p=A,B} H^{(p)}_{chain} \right),$$
$$Q_- = \frac{1}{V}\int d\vec{r} e^{-\omega_-(\vec{r})} \tag{A3}$$

with

$$H^{(p)}_{chain} = \int_0^{N_p} dt \left[\frac{3}{2b_p^2}\left(\frac{d\vec{R}^p(t)}{dt} \right)^2 + \omega_p^{eff}(\vec{R}^p(t)) \right]$$

$$\omega_p^{eff}(\vec{r}) = \omega_p(\vec{r}) - \delta_{p,A} \ln\left(1 + e^{-\omega_+(\vec{r})}\right) \tag{A4}$$

Note that the effective field for polymer A, ω_A^{eff}, includes the conjugate fields for the charge-neutral chains ω_A and for the Li^+ ions ω_+. Q_c can be written in terms of the one-end-integrated propagators, q_p and q_p^+, as (31)

$$Q_c = \frac{1}{V}\int d\vec{r} q_p^+(\vec{r}, N_p) \ , \tag{A5}$$

where q_p^+ is obtained from solving the modified diffusion equation,

$$\frac{\partial q_p^+(\vec{r},t)}{\partial t} = \frac{b_p^2}{6}\nabla^2 q_p^+(\vec{r},t) - \omega_p^{eff}(\vec{r},t) q_p^+(\vec{r},t) \tag{A6}$$

with the initial conditions, $q_A^+(\vec{r},0) = q_B(\vec{r},N_B)$ and $q_B^+(\vec{r},0) = q_A(\vec{r},N_A)$. A similar equation holds for $q_p(\vec{r},t)$, with the initial condition, $q_p(\vec{r},0) = 1$.

Making the saddle-point approximation, $\delta F/\delta\Omega = 0$, using eqn (13) leads to the following self-consistent field equations for each of the listed field variables,

$$\delta c_+ : \omega_+(\vec{r}) = \psi(\vec{r})[1 - x(\vec{r})] - \mu + \nu_- x(\vec{r})\eta(\vec{r}) - \frac{l_0 x(\vec{r})}{2a\varepsilon_r(\vec{r})} - x(\vec{r})\ln\left\{ \frac{c_0[1 - x(\vec{r})]^2}{x(\vec{r})\xi_-} \right\} + \{\chi_1 v_A[1 - x(\vec{r})] + \chi_2 v_A x(\vec{r})\}\phi_B(\vec{r})$$

$$\delta c_- : \omega_-(\vec{r}) = -\psi(\vec{r}) + \nu_-\eta(\vec{r}) + \frac{l_0}{2a\varepsilon_r(\vec{r})} + \ln\left\{ \frac{c_0[1 - x(\vec{r})]^2}{x(\vec{r})\xi_-} \right\}$$

$$\delta\phi_A : \omega_A(\vec{r}) = \nu_A\eta(\vec{r}) + \chi\nu_A\phi_B(\vec{r}) - \frac{\varepsilon_A l_0 \nu_A c_-(\vec{r})}{2a\varepsilon_r^2(\vec{r})} - \frac{\varepsilon_A \nu_A}{8\pi l_0}|\nabla\psi(\vec{r})|^2$$

$$\delta\phi_B : \omega_B(\vec{r}) = \nu_B\eta(\vec{r}) - \frac{\varepsilon_B l_0 \nu_B c_-(\vec{r})}{2a\varepsilon_r^2(\vec{r})} - \frac{\varepsilon_B \nu_B}{8\pi l_0}|\nabla\psi(\vec{r})|^2 + \nu_B\{\chi\phi_A(\vec{r}) + \chi_1[1 - x(\vec{r})]\nu_A c_+(\vec{r}) + \chi_2 x(\vec{r})\nu_A c_+(\vec{r})\}$$

$$\delta\eta : \sum_\alpha \phi_\alpha(\vec{r}) = 1$$

$$\delta\omega_+ : c_+(\vec{r}) = \frac{\phi_A(\vec{r})e^{-\omega_+(\vec{r})}}{v_A(1+e^{-\omega_+(\vec{r})})}$$

$$\delta\omega_- : c_-(\vec{r}) = \left(\frac{n_-}{V}\right)\frac{e^{-\omega_-(\vec{r})}}{Q_-}$$

$$\delta\omega_A : \phi_A(\vec{r}) = \frac{n_c v_A}{VQ_c}\int_0^{N_A} dt\; q_A^+(\vec{r},t)q_A(\vec{r},N_A-t)$$

$$\delta\omega_B : \phi_B(\vec{r}) = \frac{n_c v_B}{VQ_c}\int_0^{N_B} dt\; q_B^+(\vec{r},t)q_B(\vec{r},N_B-t)$$

$$\delta\psi : \nabla\cdot[\varepsilon_r(\vec{r})\nabla\psi(\vec{r})] = -4\pi l_0\{c_+(\vec{r})[1-x(\vec{r})] - c_-(\vec{r})\}$$

$$\delta x : \frac{n_{IP}}{(n_+ - n_{IP})(n_- - n_{IP})} = \frac{\exp[E_b + (\chi_1-\chi_2)v_A\phi_B(\vec{r}) + V_{Born}]}{\xi_- V}, \quad (A7)$$

where $n_{IP} = \int d\vec{r}x(\vec{r})c_+(\vec{r})$. The equations are obtained by the vanishing of the functional derivatives with respect to the variables on the left of the colon.

Combining the equations for c_- and ω_-, we see that the concentration of the anions is given by the Boltzmann factor $\exp[-\omega_-(\vec{r})]$, with the effective potential field $\omega_-(\vec{r})$ including the electrostatic potential, the incompressibility field, and the Born energy. The ratio of the anion concentrations at two spatial locations $\vec{r}_1$ and $\vec{r}_2$ is

$$\frac{c_-(\vec{r}_1)}{c_-(\vec{r}_2)} = e^{-\Delta\omega_-}, \quad (A8)$$

where $\Delta\omega_- = \omega_-(\vec{r}_1) - \omega_-(\vec{r}_2)$. Substituting the expression for the field ω_- gives eqn (23).

Appendix B: expansion of the free energy around the disordered phase

Writing the field variables in terms of deviation from their values in the homogeneous state [eqn (20)], we expand $\ln Q_c$, and $\ln Q_-$ to quadratic order in the deviatory field variables in Fourier space as

$$\begin{aligned}\ln Q_c \sim \ln \overline{Q}_c &+ \frac{N_A^2}{2V}\int\frac{d\vec{k}}{(2\pi)^3}\, g_A(R_A^2k^2)\delta\omega_A^{eff}(\vec{k})\delta\omega_A^{eff}(-\vec{k})\\ &+ \frac{N_B^2}{2V}\int\frac{d\vec{k}}{(2\pi)^3}\, g_B(R_B^2k^2)\delta\omega_B(\vec{k})\delta\omega_B(-\vec{k})\\ &+ \frac{N_A N_B}{V}\int\frac{d\vec{k}}{(2\pi)^3}\, g_{AB}(R_A^2k^2, R_B^2k^2)\\ &\times\delta\omega_A^{eff}(\vec{k})\delta\omega_B(-\vec{k})\end{aligned}$$

$$\ln Q_- \sim \int\frac{d\vec{k}}{(2\pi)^3}\left(\frac{n_-}{2V}\right)\delta\omega_-(\vec{k})\delta\omega_-(-\vec{k}). \quad (B1)$$

In eqn (B1), $g_p(x) = 2(x - 1 + e^x)/x^2$ (p = A, B) is the Debye function, and $g_{AB}(x, y) = (1 - e^{-x})(1 - e^{-y})/(xy)$ is the two-point cross correlation function for the two blocks in a non-interacting diblock chain. Here, $R_p^2 = N_p b_p^2/6$ is the mean square radius of gyration for block P. Inserting eqn (B1) into eqn (13) and expanding F to the quadratic order, we obtain

$$\Delta F^{(2)} = \Delta F_0^{(2)} + \Delta F_{\chi-shift}^{(2)} + \Delta F_{ion-ion}^{(2)} + \Delta F_{Born}^{(2)}, \quad (B2)$$

where $\Delta F_0^{(2)}$, $\Delta F_{\chi-shift}^{(2)}$, $\Delta F_{ion-ion}^{(2)}$ and $\Delta F_{Born}^{(2)}$ are respectively, contribution due to the intrinsic thermodynamics of the salt-free block copolymer, contribution due to altered monomer identity due to Li^+ binding to the PEO, contribution due to Coulomb interaction and entropy (translational entropy of the anions and combinatorial entropy of Li^+ binding), and contribution due to the solvation energy of the anions.

$$\begin{aligned}\Delta F_0^{(2)} = \int\frac{d\vec{k}}{(2\pi)^3}\Bigg[&-\frac{f_c^2 N_c\rho_{avg}}{2}g_A(R_A^2k^2)\;\delta\omega_A^{eff}(\vec{k})\delta\omega_A^{eff}(-\vec{k})\\ &-\frac{(1-f_c)^2N_c\rho_{avg}}{2}g_B(R_B^2k^2)\delta\omega_B(\vec{k})\delta\omega_B(-\vec{k})\\ &-f_c(1-f_c)N_c\rho_{avg}g_{AB}(R_A^2k^2, R_B^2k^2)\delta\omega_A^{eff}(\vec{k})\delta\omega_B(-\vec{k})\\ &-\rho_A\delta\omega_A^{eff}(\vec{k})\delta\phi_A(-\vec{k}) - \rho_B\delta\omega_B(\vec{k})\delta\phi_B(-\vec{k})\\ &+\chi\delta\phi_A(\vec{k})\delta\phi_B(-\vec{k})\Bigg]\end{aligned}$$

$$\Delta F_{\chi-shift}^{(2)} = v_A\chi_1\delta c_+(\vec{k})\delta\phi_B(-\vec{k})$$

$$\begin{aligned}\Delta F_{ion-ion}^{(2)} = \int\frac{d\vec{k}}{(2\pi)^3}\Bigg\{ &-\frac{\bar{\varepsilon}_r k^2}{8\pi l_0}\delta\psi(\vec{k})\delta\psi(-\vec{k})\\ &+[\delta c_+(\vec{k}) - \delta c_-(\vec{k})]\delta\psi(-\vec{k})\\ &-\frac{c_0}{2}(1-r)\delta\omega_+(\vec{k})\delta\omega_+(-\vec{k}) + r\rho_A\delta\phi_A(\vec{k})\delta\omega_+(-\vec{k})\\ &-\sum_{\gamma=+,-}\delta c_\gamma(\vec{k})\delta\omega_\gamma(-\vec{k}) - \frac{c_0}{2}\delta\omega_-(\vec{k})\delta\omega_-(-\vec{k})\Bigg\}\end{aligned}$$

$$\begin{aligned}\Delta F_{Born}^{(2)} = \int\frac{d\vec{k}}{(2\pi)^3}\Bigg[&-\frac{l_0(\varepsilon_A-\varepsilon_B)}{2a\bar{\varepsilon}_r^2}\delta\phi_A(\vec{k})\delta c_-(-\vec{k})\\ &+\frac{l_0c_0(\varepsilon_A-\varepsilon_B)^2}{2a\bar{\varepsilon}_r^3}\delta\phi_A(\vec{k})\delta\phi_A(-\vec{k})\Bigg]. \quad (B3)\end{aligned}$$

In these equations, $\bar{\varepsilon}_r = \varepsilon_A\overline{\phi}_A + \varepsilon_B\overline{\phi}_B$ is the dielectric constant of the mixture in the homogeneous state. For convenience, we have introduced $\rho_A = 1/v_A$, $\rho_B = 1/v_B$, and $\rho_{avg} = 1/[f_c v_A + (1-f_c)v_B]$. Note that, within the simple Born model, the effect of the anion solvation energy $\Delta F_{Born}^{(2)}$ vanishes when the dielectric constants of the two blocks are the same, that is $\varepsilon_A = \varepsilon_B$.

To obtain the an effective free energy as a functional of the polymer density $\delta\phi_p(\vec{k})$ only, eqn (22), we perform the functional

integral in eqn (19) over field variables other than $\delta\phi_p(\vec{k})$. Because the integrals are Gaussian, the calculation can also be done simply by extremizing the integrand with respect to the field variables. We first integrate over the effective field variables to obtain

$$\delta\omega_{\mathrm{A}}^{\mathrm{eff}}(\vec{k}) = [-\rho_{\mathrm{A}}\delta\phi_{\mathrm{A}}(\vec{k}) - f_{\mathrm{c}}N_{\mathrm{c}}\rho_{\mathrm{avg}}g_{\mathrm{AB}}\delta\omega_{\mathrm{B}}(\vec{k}) + f_{\mathrm{c}}^2N_{\mathrm{c}}\rho_{\mathrm{avg}}g_{\mathrm{AB}}\delta\omega_{\mathrm{B}}(\vec{k})] \times \left(\frac{1}{f_{\mathrm{c}}^2N_{\mathrm{c}}\rho_{\mathrm{avg}}g_{\mathrm{A}}}\right)$$

$$\delta\omega_{\mathrm{B}}(\vec{k}) = \frac{(\rho_{\mathrm{B}}f_{\mathrm{c}}g_{\mathrm{A}} + g_{\mathrm{AB}}\rho_{\mathrm{A}} - g_{\mathrm{AB}}\rho_{\mathrm{A}}f_{\mathrm{c}})\delta\phi_{\mathrm{A}}(\vec{k})}{f_{\mathrm{c}}N_{\mathrm{c}}\rho_{\mathrm{avg}}(1-f_{\mathrm{c}})^2(g_{\mathrm{A}}g_{\mathrm{B}} - g_{\mathrm{AB}}^2)}$$

$$\delta\omega_{+}(\vec{k}) = \frac{[\rho_{\mathrm{A}}r\delta\phi_{\mathrm{A}}(\vec{k}) - \delta c_{+}(\vec{k})]}{c_0(1-r)}$$

$$\delta\omega_{-}(\vec{k}) = -\frac{\delta c_{-}(\vec{k})}{c_0}.$$

$$\delta\psi(\vec{k}) = \left(\frac{4\pi l_0}{k^2\bar{\varepsilon}_r}\right)\left[\delta c_{+}(\vec{k}) - \delta c_{-}(\vec{k})\right]. \quad \text{(B4)}$$

We recognize that the last equation for the electrostatic field is just the Poisson equation. Note that these equations establish a linear relationship between the effective fields and the density fields. Thus, the Gaussian fluctuation approximation is equivalent to the linear response theory (or the random phase approximation)(35). Finally for the Gaussian integral of the ion densities, we further minimize $\Delta F^{(2)}$ with respect to $\delta c_{\gamma}(\vec{k})$ ($\gamma = \pm$), together with eqn (B4). This leads to

$$\delta c_{-}(\vec{k}) = \frac{l_0c_0[r\Delta\varepsilon_{\mathrm{r}}\delta\phi_{\mathrm{A}}(\vec{k})k^2 + 8\pi\varepsilon_{\mathrm{r}}a\delta c_{+}(\vec{k})]}{2\bar{\varepsilon}_{\mathrm{r}}a(k^2\bar{\varepsilon}_{\mathrm{r}} + 4\pi l_0c_0)}$$

$$\delta c_{+}(\vec{k}) = \left[-4\pi l_0c_0(1-r) - 4\pi l_0c_0 - k^2\bar{\varepsilon}_{\mathrm{r}}\right]^{-1} \times \Big[-2\pi l_0^2c_0^2\rho_{\mathrm{A}}r\Delta\varepsilon_{\mathrm{r}} + 2\pi l_0^2c_0^2\rho_{\mathrm{A}}r\Delta\varepsilon_{\mathrm{r}} - 4\pi l_0c_0^2\chi_1\bar{\varepsilon}_r^2a(1-r) - 4\pi l_0\bar{\varepsilon}_r^2a\rho_{\mathrm{A}}^2rc_0 + \chi_1c_0 - c_0\chi_1\bar{\varepsilon}_{\mathrm{r}}^3ak^2(1-r) - \bar{\varepsilon}_{\mathrm{r}}^3a\rho_{\mathrm{A}}^2rk^2\Big]\delta\phi_{\mathrm{A}}(\vec{k}). \quad \text{(B5)}$$

All field variables are now expressed solely in terms $\delta\phi_{\mathrm{A}}(\vec{k})$. Combining eqn (B3)–(B5), we obtain $\Delta F^{(2)}$ in eqn (B2) in the form of the quadratic functional of $\delta\phi_{\mathrm{A}}(\vec{k})$, eqn (22)

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